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The almost hidden role of deep traps when measuring afterglow and thermoluminescence of persistent phosphors

David Van der Heggen [a], Dimitri Vandenberghe [b], Nasrin K. Moayed [b], Johan De Grave [b], Philippe F. Smet [a], Jonas J. Joos [a,*]

[a] LumiLab, Department of Solid State Sciences, Ghent University, Krijgslaan 281 (S1), 9000 Gent, Belgium
[b] Laboratory of Mineralogy and Petrology, Department of Geology, Ghent University, Krijgslaan 281 (S8), 9000 Gent, Belgium

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ABSTRACT

Although the luminescence characteristics of persistent phosphors have been extensively investigated, the physical mechanism underlying their afterglow is not yet fully understood. Many variables influence the outcome of thermoluminescence, charging and afterglow experiments, hampering a correct interpretation. Here we investigate the role of deep, thermally stable traps in $SrAl_2O_4$:Eu^{2+},Dy^{3+} which received little attention in previous studies. We demonstrate that these traps have a considerably higher trapping cross-section than the shallow traps, which are responsible for the persistent luminescence. This affects the charging dynamics of the shallow traps significantly and should therefore be considered in behavioral studies of these phosphors.

1. Introduction

The discovery by Matsuzawa et al. [1] that codoping with dysprosium significantly improves the persistent luminescence duration and intensity of $SrAl_2O_4$:Eu^{2+} marked the beginning of a period of extensive research into luminescent properties of rare-earth doped aluminates and silicates [2–4]. Thermoluminescence (TL) is a popular technique to investigate the characteristics of traps and trap distributions [5,6]. It should thus be ideally suited to uncover the workings of the persistent luminescence in these materials. The interpretation of the data, however, has proven to be not so straightforward. The shape and intensity of the glow curves depend on the excitation temperature and wavelength as well as the dopant concentrations of the phosphors [7]. Moreover, the use of expressions relying on numerous, often mutually correlated, parameters complicate the interpretation in terms of microscopic models.

In what follows, we will present evidence for the existence of deep traps in $SrAl_2O_4$:Eu^{2+},Dy^{3+} that are obscured by thermal quenching (TQ) and have hardly been studied. Deep traps are useful in many applications such as dosimetry or optical memory storage [8,9] but given their depth they could be expected to have little or no influence on the afterglow properties of $SrAl_2O_4$:Eu^{2+},Dy^{3+} at room temperature [10]. However, as we show, the initial filling rate of the shallow traps responsible for the afterglow, is greatly influenced by these deep traps.

2. Experimental

All measurements were performed on commercial $SrAl_2O_4$:Eu^{2+},Dy^{3+} powder (GloTech Int.). The TL measurements were performed using an automated Risø TL/OSL reader equipped with blue (λ_{max} = 470 nm, FWHM = 32 nm) light emitting diodes (LEDs) providing an excitation intensity of 0.55 mW/cm^2 at sample position. Stimulation with green light was achieved using a frequency-doubled Nd:YAG laser (λ = 532 nm) which was coupled to the setup using optical fibers resulting in a stimulation intensity of 0.25 mW/cm^2 at the sample position. All glow curves were recorded while heating at a rate of 1 °C/s under a nitrogen atmosphere. A combination of a Schott BG39 and a Schott BG3 filter was used in front of the PMT, enabling detection of the green TL signal [11,12]. Excitation of the phosphor was always carried out at room temperature using blue light. No ionizing radiation has been used and the term "dose" is used to reflect the amount of blue light to which the sample has been exposed. A S401C thermal power sensor (Thorlabs) was used to measure the intensity of the illumination sources.

The thermal quenching profile was measured in a home built setup using a resistive heating element to heat the sample at a rate of 0.5 °C/s, with temperature feedback using a USB-6002 DAQ device (National Instruments). A 5 mm blue LED (λ_{max} = 450, FWHM = 30 nm) driven at 20 mA was used as an excitation source and the emission spectra were measured using a QE65000 spectrometer (Ocean Optics).

* Corresponding author.
E-mail address: jonas.joos@ugent.be (J.J. Joos).

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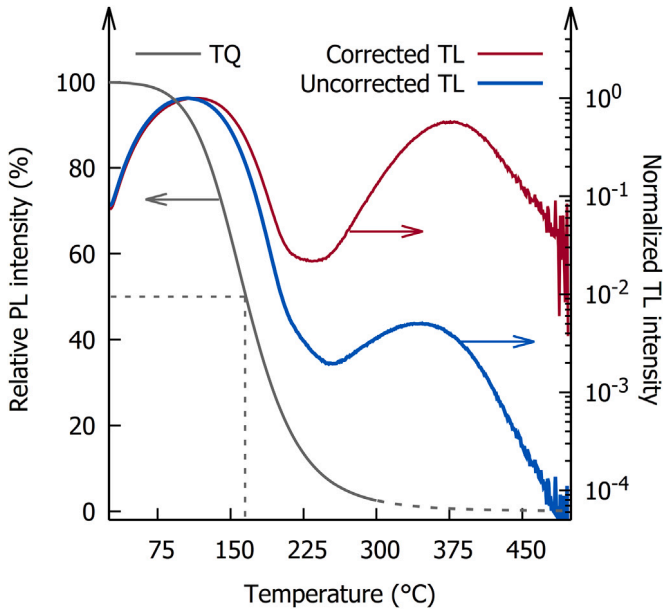

Fig. 1. TL glow curve (as-measured and corrected for TQ) of $SrAl_2O_4$:Eu,Dy recorded after 5 s of illumination with blue light at a heating rate of 1 °C/s. The TQ profile used to correct the TL measurements is also shown and the $T_{0.5}$ is indicated. The dashed line indicates the extrapolation of the TQ profile according to the fit. Please note that the TQ profile is shown on a linear scale (left) while the TL curves are reproduced on a logarithmic scale (right).

3. Results and discussion

The TL glow curve of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ following 5 s of illumination with blue light is shown in Fig. 1. The as-measured glow curve is characterized by a low temperature peak, located around 110 °C, which is responsible for the phosphor's well-known afterglow and is the subject of many investigations [1,13–16]. However, in order to reflect the correct amount of detrapped charges the thermoluminescence measurements should be corrected for TQ [5]. Obtaining quantitative information about TQ is not straightforward for persistent phosphors due to trapping and detrapping processes that can induce artifacts in the TQ profile [13]. To suppress these effects the TQ profile was recorded twice: once while heating to 300 °C and again while cooling back to room temperature. The acquired profile was then fit by a phenomenological single barrier model [17]:

$$I(T) = \frac{I(0)}{1 + A\,\exp\left(\frac{-\Delta E_{TQ}}{kT}\right)} \quad (1)$$

where $I(T)$ represents the intensity at temperature T, A is a constant, k is the Boltzmann constant and ΔE_{TQ} is the activation energy for thermal quenching. The resulting quenching temperature, i.e. the temperature at which the intensity drops to 50% of its original value ($T_{0.5}$), was found to be 165 °C and is in line with previous reports [18]. As shown by Fig. 1, correcting the glow curve for TQ emphasizes a second, significant TL peak located around 375 °C, which is hardly noticeable in the uncorrected profile, especially when plotted on a linear scale. It is therefore only mentioned in a limited number of reports [19–22].

It should be pointed out that this correction tacitly assumes that both TL glow peaks share the same recombination center [23]. However, taking into account that trapping is induced after direct excitation of Eu^{2+} with blue light it seems improbable that a second recombination center would play an important role. For the remainder of the article, all shown results are corrected for TQ.

Thermoluminescence measurements or thermal cleaning steps are often only performed up to temperatures around 200 or 250 °C to limit the experimental overhead or due to technical limitations. This temperature is sufficiently high to record the low temperature glow curve but does not affect the charges trapped in the deep traps. It is known that different trapping centers can interact [24–27], suggesting that the deep traps might, even at room temperature, affect the afterglow mechanism. In the following, the impact of this hidden variable on the persistent luminescence properties will be elucidated.

For this, a TL experiment was devised which is schematically represented in Fig. 2(a). Every experiment consists of n consecutive cycles during which the phosphor is illuminated with blue light and subsequently heated to only 250 °C, allowing to record the low temperature TL peak (blue arrows in Fig. 2(a)). These n cycles are followed by a final heating to 500 °C which allows to record the high temperature TL peak after n illumination cycles (red arrow in Fig. 2(a)).

For the first series of experiments the illumination time was kept fixed at 1 s and the number of illumination and preheating cycles n was varied from 1 to 7. The low and high temperature TL curves are shown in Fig. 2(b) and Fig. 2(c), respectively. The intensity of the low temperature TL peak increases with n and at the same time the maximum of the glow curve shifts to higher temperatures. The shift of the glow curve can be understood by taking into account that the low temperature peak is not due to a single trap but is the result of an underlying trap depth distribution [6,13,20]. The increase in intensity is, however, unexpected because heating to 250 °C empties all shallow traps related to the low temperature glow curve and therefore no build-up of charges is expected between successive cycles. This was verified by heating the phosphor twice to 250 °C without any intermediate illumination. There was no detectable TL signal during the second heating cycle, demonstrating that the shallow traps are indeed completely emptied after heating to 250 °C. The intensity of the high temperature TL peak increases with n as well and simultaneously the peak shifts to lower temperatures. This increase in intensity is not surprising, considering that the deep traps are not emptied during preheating to 250 °C.

If the preheat temperature is raised to 500 °C instead of 250 °C, thereby emptying both shallow and deep traps after every illumination, the intensity of both peaks remains constant (see Fig. 3). Therefore we can conclude that the anomalous increase in TL intensity of the low temperature glow curve is related to the occupation of the deep traps which gives rise to the high temperature glow curve. This experiment shows that seemingly non-reproducible results are obtained if the effect of the deep traps is ignored.

One possible mechanism that can explain our findings is that trapped carriers are optically reshuffled, i.e. a redistribution of the trap occupations takes place during every illumination step. In this scenario the excitation light induces a net transfer of trapped charges from the deep to the shallow traps. Optically stimulated detrapping has been identified before as a major cause for the limited storage capacity of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ [28]. Moreover a similar effect has been reported in chromium doped lithium and zinc gallates [24–26] and $BaSi_2O_2N_2:Eu^{2+}$ [27].

Detecting an optical rearrangement of trap occupation under illumination with blue light is complicated by the fact that this light also excites Eu^{2+} and contributes to the trap filling. Experiments by Jia et al. [29] indicate that OSL can be induced with ultraviolet, green or infrared light, implying that excitation of Eu^{2+} can be overcome by using green instead of blue light to induce the transfer of trapped charges from the deep to the shallow traps. The activation energy needed to induce this transfer will be considerably lower than the energy needed to induce an electron transfer from the deep trap to the activator ion. Hence, the comparison of results obtained using stimulation with green and blue light is not expected to be significantly affected by the small difference in photon energy [30,31]. The phosphor was therefore first exposed to blue light to induce trap filling, subsequently preheated to 250 °C to empty the shallow traps and then exposed to green light with wavelength of λ = 532 nm and a comparable intensity to the

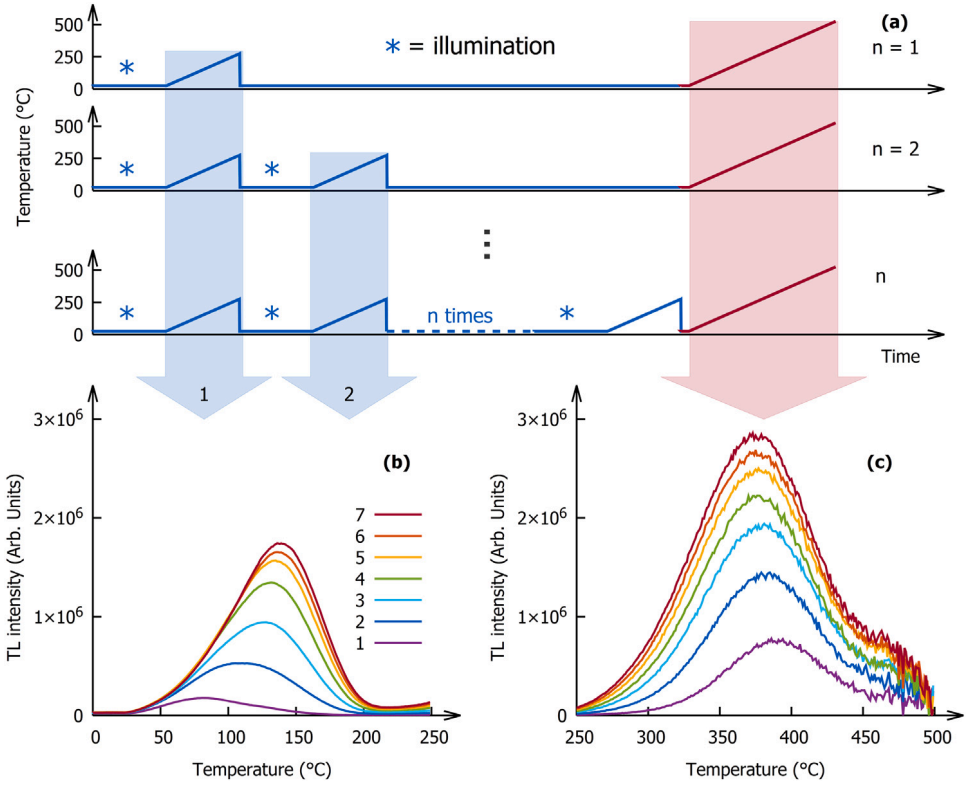

Fig. 2. (a) Outline of the TL experiments performed on $SrAl_2O_4$:Eu,Dy. Every experiment consists of n illumination and preheating (to 250 °C) cycles followed by a final heating to 500 °C. (b) Thermoluminescence glow curves recorded during seven (n = 7) consecutive illumination and preheating cycles as indicated by the blue arrows in Fig. 2(a). No intermediate heating to 500 °C took place. (c) High temperature TL glow curves measured after n (ranging from 1 to 7) consecutive illumination and preheating cycles as indicated by the red arrow in Fig. 2(a). All glow curves were recorded at a heating rate of 1°C/s and corrected for thermal quenching. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

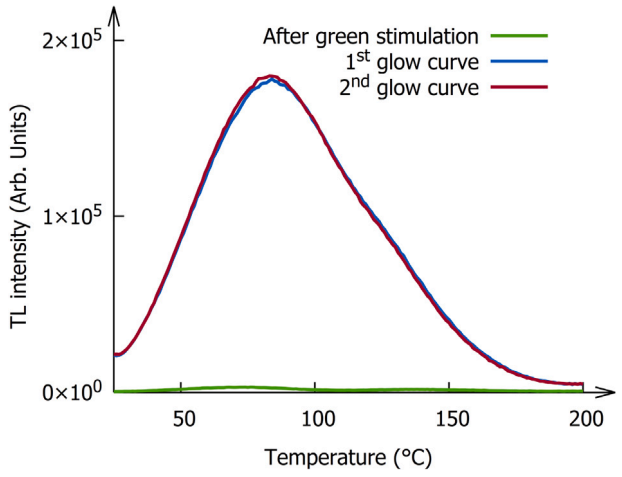

Fig. 3. Low temperature glow curves recorded after 1 s of illumination with blue light. The curves were measured consecutively with an intermediate heating to 500 °C. The green curve is recorded after the sample was exposed to blue light for 1 s, subsequently heated to 250 °C and then illuminated by green light during 10 s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

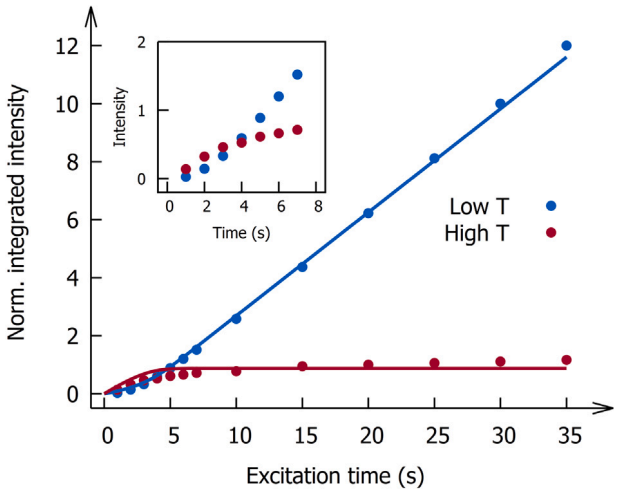

Fig. 4. Integrated TL intensity of the low (RT-250 °C) and high temperature (250–500 °C) glow peaks of $SrAl_2O_4$:Eu,Dy after exposure to blue light. The inset emphasizes the sublinear filling of the shallow traps at low excitation times.

blue excitation light. A measurement of the TL, shown in Fig. 3, indicates that the green light indeed induces a transfer of trapped charges from deep to shallow trapping centers but the effect is about 200 times smaller than the effect under blue illumination. It can hence be concluded that an optical redistribution of the trap occupation is most likely not at the origin of the effect shown in Fig. 2.

Alternatively, a competition between the deep and shallow traps during the filling might explain the anomalous increase in intensity of the low temperature peak. If that is the case, illumination with blue light leads to a preferential filling of the deep traps, followed by a subsequent, increasingly rapid filling of the shallow traps.

The integrated glow curve intensities as a function of excitation time are shown in Fig. 4. From the figure it is clear that the filling of the shallow traps is sublinear during the first few seconds of illumination

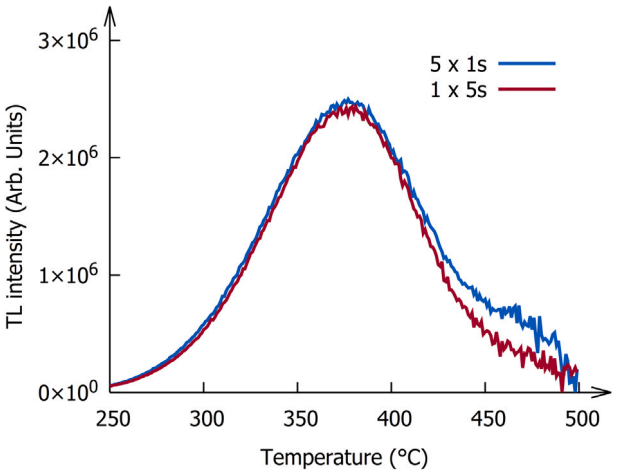

Fig. 5. High temperature TL glow curves of a sample that was exposed to blue light for a total of 5 s. Either in one illumination-preheat cycle ($n = 1$, red curve) or divided over five such cycles ($n = 5$, blue curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and speeds up once the deep traps reach saturation. It is during these first seconds that the peculiar behavior shown in Fig. 2 is visible. Assuming, for simplicity, that the distribution of traps giving rise to the low temperature TL peak can here be approximated by a single trap, the dose dependency of the trap filling can be modeled with a simple two trap model (see Fig. 4),

$$\frac{dn_i}{dt} = I\frac{\left(n_{i,0} - n_i\right)\sigma_i}{\left(n_{s,0} - n_s\right)\sigma_s + \left(n_{d,0} - n_d\right)\sigma_d} \quad (2)$$

where i can be equal to d or s referring to the deep or shallow traps respectively, I represents the excitation rate, $n_{s,0}$ and $n_{d,0}$ the total number of traps and σ_s and σ_d represent their trapping cross-sections. A qualitative agreement with the experiment can only be achieved if the trapping probability, i.e. the product of the trapping cross-section and the trap density, of the deep traps is around two times larger compared to the trapping probability of the shallow traps. Since it is evident from Fig. 4 that the density of shallow traps is appreciably larger than the density of deep traps, this implies that the deep traps have a much larger trapping cross-section than the shallow traps. Because information of the physical path that leads to trapping is not available, the trapping cross-section as presented here represents the combined trapping cross-section of all the processes that take place between excitation of the activator and the filling of the trap.

As a result of this observation, it is expected that the filling of the deep traps is independent from the occupation of the shallow traps. To demonstrate this, two distinct glow curves of the deep trap are compared (Fig. 5), both obtained after accumulating 5 s of illumination, either in one illumination-preheat cycle ($n = 1$, 5 s illumination time) or divided over five such cycles ($n = 5$, 1 s illumination time). In the latter experiment the shallow traps are emptied 5 times during the pre-heat steps whereas in the former no intermediate emptying of the shallow traps takes place, resulting in different occupations of the shallow traps for the two experiments. Fig. 5 shows that the resulting high temperature glow curves are almost identical, confirming that the filling of the deep traps is indeed independent of the occupation of the shallow traps.

Additionally, the cumulative intensity of the low temperature glow curves is identical in both experiments. This in turn implies that the filling rate of the shallow traps is not affected by their occupation, but that it is only governed by the occupation of the deep traps, at least at the examined illumination intensities which are sufficiently low to avoid saturation effects.

4. Conclusions

In summary, a deep trap in the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ persistent phosphors was identified and characterized. Its signature is well-hidden by thermal quenching, making it largely overlooked. In contrast to its low visibility, it was shown that it can have a far-reaching impact on a range of experiments that probe the persistent luminescence behavior of phosphors. This is of special importance for experiments which are not carried out under steady state equilibrium conditions such as modeling efforts to reproduce the charging curves during excitation or dose dependent TL investigations. As long as the filling of the deep traps has not yet reached saturation their presence greatly influences the filling rate of the shallow traps responsible for the phosphor's afterglow.

We demonstrated that the mechanism behind these effects is a preferential filling of the deep traps with respect to the shallow traps responsible for the afterglow. Keeping the phosphor in the dark for several hours or heating to temperatures below 500 °C does not ensure that the phosphor is in pristine condition, i.e. with all traps emptied, and can considerably affect the resulting charging dynamics.

CRediT authorship contribution statement

David Van der Heggen: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization, Project administration, Funding acquisition. **Dimitri Vandenberghe:** Methodology, Investigation, Resources, Writing - review & editing, Supervision, Project administration. **Nasrin K. Moayed:** Investigation, Writing - review & editing. **Johan De Grave:** Writing - review & editing, Resources. **Philippe F. Smet:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Funding acquisition. **Jonas J. Joos:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Project administration, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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